

BERYLLIUM AND CERTAIN BERYLLIUM COMPOUNDS

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CARCINOGENICITY

Beryllium (CAS No. 7440-41-7) and the following beryllium compounds: beryllium-aluminum alloy (12770-50-2), beryllium chloride (7787-47-5), beryllium fluoride (7787-49-7), beryllium hydroxide (13327-32-7), beryllium oxide (1304-56-9), beryllium phosphate (13598-15-7), beryllium sulfate (13510-49-1), beryllium sulfate tetrahydrate (7787-56-6), beryllium zinc silicate (39413-47-3), and beryl ore (1302-52-9) are *reasonably anticipated to be human carcinogens* based on sufficient evidence of carcinogenicity in experimental animals (IARC V.1, 1972; IARC V.23, 1980; IARC S.4, 1982). Beryllium metal, beryllium-aluminum alloy, beryl ore, beryllium chloride, beryllium fluoride, beryllium hydroxide, beryllium sulfate (and its tetrahydrate) and beryllium oxide all produced lung tumors in rats exposed by inhalation or intratracheally. Single intratracheal instillations or 1-hour inhalation exposures were effective. Beryllium oxide and beryllium sulfate produced lung anaplastic carcinomas in monkeys after intrabronchial implantation or inhalation. Beryllium metal, beryllium carbonate, beryllium oxide, beryllium phosphate, beryllium silicate, and zinc beryllium silicate all produced osteosarcomas in rabbits after intravenous and/or intramedullary administration.

There is limited evidence for the carcinogenicity of beryllium in humans (IARC V.23, 1980; IARC S.4, 1982; IARC S.7, 1987). There were no data available to evaluate the carcinogenicity of beryllium compounds in humans. Four early epidemiological studies and three recent studies of occupational exposure to beryllium were considered to provide limited evidence that exposure to beryllium may lead to human lung cancer. The data for most of the studies were derived from two beryllium plants and from the Beryllium Case Registry. Although 55 new cases of beryllium disease were registered between 1973 and 1977, no further data were available on the incidence of lung cancer. An analysis of the pathology of the 47 lung cancers noted in one study confirmed the post-mortem diagnoses of lung cancer in 32 of the 37 cases available for review. Of the 47 cases, 21 were reported smokers, but the smoking histories of individuals in the other cases were not given (IARC S.4, 1982).

PROPERTIES

Beryllium is a grey metal with a close-packed hexagonal crystal structure. It is insoluble in cold water and mercury, slightly soluble in hot water, in which it decomposes, and soluble in dilute acids and alkalis. Beryllium chloride occurs as white-to-colorless deliquescent crystals. It is very soluble in cold and hot water; soluble in alcohol, benzene, ether, chloroform, and carbon disulfide; and insoluble in ammonia and acetone. Beryllium fluoride occurs as a colorless amorphous mass that is readily soluble in water but only slightly soluble in alcohol. Beryllium hydroxide exists in three forms: as a metastable tetragonal crystalline solid; as a stable orthorhombic crystalline solid; and in a slightly basic pH, it appears as a slimy, gelatinous substance. It is soluble in acids and alkalis but insoluble in water. Beryllium oxide (BeO) occurs as a white amorphous powder or gel which is insoluble in both cold and hot water but is soluble in acids, alkalis, and ammonium carbonate. Beryllium metaphosphate is a white porous powder or granular material that is insoluble in water. Beryllium orthophosphate is soluble in both cold and hot water and acetic acid. Beryllium sulfate occurs as colorless crystals which are insoluble in cold water and alcohol but decompose in hot water. Beryllium sulfate tetrahydrate occurs as crystals that are soluble in water, practically insoluble in ethanol, and slightly soluble in concentrated sulfuric acid. Beryl ore is a colorless, blue-green, yellow, or white, transparent,

hexagonal crystal that is insoluble in acid. When heated to decomposition, beryllium, beryllium-aluminum alloy, beryllium chloride, beryllium fluoride, beryllium hydroxide, beryllium oxide, beryllium sulfate, and beryllium sulfate tetrahydrate emit toxic fumes of BeO. In addition, beryllium chloride emits toxic fumes of hydrochloric acid and other chlorinated compounds, beryllium fluoride emits toxic fumes of hydrofluoric acid and other fluorinated compounds, beryllium phosphate emits toxic fumes of phosphorus oxides (PO_x), and beryllium sulfate and beryllium sulfate tetrahydrate emit toxic fumes of sulfur oxides (SO_x).

Beryllium metal is available in the United States as a technical grade with over 99.5% purity, as a commercial grade with 97% minimum purity, and as an electro-refined metal in various grades, i.e., vacuum hot pressed S-200, S-65, and I-40. Beryllium chloride and beryllium fluoride are available with 11.2% and 19.0% beryllium content, respectively. Both contain various metallic impurities. Beryllium-aluminum alloy is available as a grade containing 62% beryllium and 38% aluminum. Beryllium hydroxide is either beryl-derived or bertrandite-derived. Depending upon the source of ore, beryllium hydroxide is available with a varying percentage of beryllium content and metallic impurities. Beryllium oxide is available as technical grade, C.P., pure, ceramic grade, and as single crystals. Commercial-grade beryllium oxide, available in the United States, has an approximate purity of 99.5%. Beryllium sulfate crystals are available with a minimum of 20% beryllium. Beryllium sulfate tetrahydrate is produced commercially in a highly purified state. Beryl ore is available in commercial grades containing 70%-90% beryl, including 10%-13% BeO.

USE

Beryl ore is processed to make beryllium and its compounds. Industry is increasing the use of beryllium for fiber optics and cellular network communication systems (USDOJ, 1990). Because it is expensive, applications will be limited to those that require light-weight, high-strength, and high-thermal conductivity. The use pattern for beryllium in 1989 was estimated to be 23% as alloy and metal for aerospace and defense; 17% as alloy and oxide for electrical components; 35% as alloy and oxide in electronic components; and 25% as alloy, metal and oxide in other applications (USDOJ, 1990). In 1987, 22% of the beryllium produced was used as an alloy and metal in aerospace applications and defense application; 36% was used as an alloy and oxide in electrical equipment; 20% was used as an alloy and oxide in electronic components; and 22% was used as compounds, alloys, and metal in other applications (USDOJ, 1988). Beryllium is used as a window material for X-ray tubes, as a moderator material for nuclear weapons, and as a neutron reflector in high-flux reactors. It is also used in high-performance aircraft brakes, in inertial guidance systems in space optics, as an additive in solid propellant rocket fuels, and in alloys (Sax, 1987; Kirk-Othmer V.3, 1978). Beryllium-aluminum alloy is not known to be produced for commercial use (IARC V.23, 1980). It has been used in light aircraft construction (Merian, 1984). It also has potential use in casting alloys, where it refines the grain size resulting in better surface polishing, reduces melt losses, and improves casting fluidity (Kirk-Othmer V.3, 1978; IARC V.23, 1980). Beryllium chloride's primary use is in the laboratory manufacture of beryllium metal by electrolysis. It also finds use as an acid catalyst in organic reactions. Beryllium fluoride and beryllium hydroxide find commercial use as intermediates in the production of beryllium metal and beryllium alloys. Beryllium fluoride is also used in the manufacture of glass and nuclear reactors (Sax, 1987). Beryllium oxide is the most important high-purity commercial beryllium chemical produced (Kirk-Othmer V.3, 1978). Its primary use is in the manufacture of ceramics. It is often used in electronic and microelectronic application, such as semiconductor devices and integrated circuits requiring thermal dissipation (IARC V.23, 1980; Kirk-Othmer V.3, 1978). Beryllium oxide is also used in the preparation of beryllium compounds, as an additive to glass and plastics, and as a catalyst for organic reactions and in high

temperature reactor systems. Beryllium oxide was used in the past for the manufacture of phosphors for fluorescent lamps. Beryllium metaphosphate has limited use as a raw material for special ceramic compositions and as a catalyst carrier. The primary use of beryllium sulfate tetrahydrate is as a chemical intermediate in the processing of beryl and bertrandite ores (Sax, 1978). A former use of beryllium zinc sulfate is as an oxygen-dominated phosphor in luminescent materials (IARC V.23, 1980; Sax, 1987).

PRODUCTION

The United States is the leading producer of beryllium ores and the leading producer and consumer of the metal, alloys, and oxide (ATSDR, 1993-R013). US beryllium mine production was 450,000 lb and imports were 110,000 lb in 1989 (USDOI 1985, 1987, 1988, and 1990).

In 1987, two U.S. companies produced beryllium alloys and beryllium oxide (USDOI, 1988). In 1985, about 3.3 million lb of beryllium ore, less than 2,532 lb of beryllium oxide, and 7,332 lb of unspecified beryllium compounds were imported (USDOC Imports, 1986). In 1984, the United States imported 2.7 million lb of beryllium ore, less than 179 lb of beryllium oxide, and 43,059 lb of unspecified beryllium compounds (USDOC Imports, 1985). The 1979 TSCA Inventory reported that in 1977, three companies produced 605,000 lb of beryllium oxide and one company imported 500 lb; two companies produced 550,000 lb of beryllium sulfate, with some site limitations; and one company produced 5.5 million lb of beryl ore. No data were reported for beryllium phosphate and beryllium zinc sulfate (TSCA, 1979). U.S. companies have produced beryllium and some beryllium compounds commercially since the 1940s and beryllium oxide since 1958 (IARC V.1, 1972).

EXPOSURE

The primary routes of potential human exposure to beryllium and certain beryllium compounds are inhalation and dermal contact. In 1970, NIOSH estimated that the number of workers potentially exposed to the dust or fumes of beryllium in the workplace was about 30,000, of which 2,500 were employed in its production (IARC V.23, 1980). The National Occupational Hazard Survey, conducted by NIOSH from 1972 to 1974, estimated that 19,867 U.S. workers may have been exposed to beryllium in the workplace (NIOSH, 1976). The National Occupational Exposure Survey (1980-1983) estimated that 19,012 total workers, including 1,778 women, may have been exposed (NIOSH, 1984). The workers potentially exposed to beryllium include beryllium ore miners, beryllium alloy makers and fabricators, phosphor manufacturers, ceramic workers, missile technicians, nuclear reactor workers, electric and electronic equipment workers, and jewelers. In addition, workers involved in fluorescent powder manufacture and in the manufacture and salvage of fluorescent lamp works were previously exposed to beryllium oxide and beryllium zinc silicate. The industry abandoned the use of these compounds because of the incidence of beryllium disease (IARC V.1, 1972). The ACGIH has adopted a threshold limit value (TLV) of 0.002 mg/m³ as an 8-hr time-weighted average (TWA) (ACGIH, 1986).

The general population is potentially exposed to trace amounts of beryllium by inhaling air and consuming food contaminated with beryllium residues. Exposure occurs mainly through the release of beryllium into the atmosphere, most likely as beryllium oxide, from the burning of coal. From 10 to 20 million lb/yr of beryllium may be emitted from coal burning and refuse incineration globally. Other anthropogenic processes include ore processing, metal fabrication, beryllium oxide production and use, and municipal waste combustion. These however, account

for a very small fraction of the amounts emitted from coal and fuel oil combustion (96%). Beryllium concentrations in U.S. coal ranges from 1.46 to 1.52 mg/kg (IARC V.23, 1980; ATSDR, 1993-R013). The EPA estimated the total release of beryllium to the atmosphere from point sources to be 5,500 lb/yr, with the principal emissions from beryllium-copper alloy production. The Toxic Chemical Release Inventory (EPA) estimated that 48,714 lb of beryllium and beryllium compounds were released to the environment from nine facilities that produced, processed, or used the compounds in the United States in 1996. Of that total, 97.4% was released to land. A facility located in Elmore, Ohio, reporting under industrial classifications for manufacture of primary nonferrous metals (SIC Code 3339) and copper rolling and drawing (SIC Code 3351) and releasing > 10,000 lb of the substances, accounted for 57.6% of the release. The amount discharged to water was < 1% (32 lb) and that to air was 2.6% (1,254 lb) (TRI96, 1998). Approximately 721,000 persons living within 12.5 miles of point sources are possibly exposed to small amounts of beryllium (median concentration, 0.005 $\mu\text{g}/\text{m}^3$). In the eastern United States, urban atmospheric concentrations were measured at 0.3 to 3.0 ng beryllium/ m^3 . In rural areas concentrations were 12 times lower. Beryllium occurs naturally in rocks and minerals with concentrations ranging from 0.038 to 11.4 mg/kg. The beryllium content of mineral oils has been estimated to be less than 100 $\mu\text{g}/\text{L}$. Small concentrations of beryllium have been reported in drinking water supplies and in food. Beryllium has also been found in tobacco (Merian, 1984). Concentrations of beryllium in cigarettes ranged from 0.47 to 0.74 mg/cigarette; 4.5 to 10% of the beryllium content escaped into the smoke during smoking (IARC V.23, 1980).

REGULATIONS

In 1980 CPSC preliminarily determined that beryllium, beryllium oxide, and beryllium sulfate was not present in consumer products under its jurisdiction. Subsequently, public comment was solicited to verify the accuracy of this information; no comments were received. Pending receipt of new information, CPSC plans no action on this chemical. In 1973 EPA promulgated a National Emissions Standard for Hazardous Air Pollutants (NESHAP) for extraction and production sites for beryllium and beryllium oxide and for beryllium rocket-motor firing. In 1980, EPA published a water quality criteria document on beryllium for the protection of human health under the Clean Water Act (CWA) and established regulations under the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) for releases of beryllium and beryllium compounds. These regulations were based on the inclusion of beryllium and its compounds on the EPA Carcinogen Assessment Group's list of potential carcinogens. The CERCLA final reportable quantity (RQ) is 10 lb for beryllium and beryllium dust and 1 lb for beryllium chloride and beryllium fluoride. RCRA subjects wastes known to contain beryllium or beryllium compounds to handling and report/recordkeeping requirements. EPA does not plan to regulate beryllium in drinking water under the Safe Drinking Water Act. Beryllium and its compounds are also regulated under the Superfund Amendments and Reauthorization Act (SARA), which subjects them to reporting requirements. FDA regulates beryllium in bottled water under the Federal Food, Drug and Cosmetics Act (FD&CA). NIOSH recommended that exposure to beryllium and beryllium compounds should not exceed 0.5 $\mu\text{g}/\text{m}^3$. Current OSHA standards for workers exposed to beryllium are a 2 $\mu\text{g}/\text{m}^3$ 8-hr TWA, 5 $\mu\text{g}/\text{m}^3$ ceiling, and 25 $\mu\text{g}/\text{m}^3$ maximum peak in 30 minutes. These standards were adopted by OSHA for toxic effects other than cancer. OSHA has proposed regulating occupational exposure to beryllium, based on its carcinogenicity as well as other toxic effects. OSHA regulates beryllium and certain beryllium compounds under the Hazard Communication Standard and as chemical hazards in laboratories. Regulations are summarized in Volume II, Table B-13.